Long-time relaxation of the magnetization in a pure crystal magnet La$_5$Mo$_4$O$_{16}$

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We found that a layered magnet La$_5$Mo$_4$O$_{16}$ exhibits a long-time relaxation of the magnetization from a ferromagnetic to an antiferromagnetic state. This unconventional relaxation in a pure crystal magnet far below the transition temperature arises from the extremely two-dimensional nature of the magnetic interactions, by which the Mo spins are strongly coupled and form a big spin within a layer.

The relaxation of magnetization has been observed in various magnetic systems, for example, magnetic nanoparticles [1,2], large magnetic molecules [3–6], diluted magnets [7,8], geometrically frustrated magnets [9–11], and magnets exhibiting a metamagnetic phase transition [12–19]. In these systems, the ac magnetic susceptibility exhibits a peculiar frequency dependence and/or the magnetization exhibits a time dependence, both of which are characterized by a relaxation-type time dependence, $M = M_0 \exp(-t/\tau)$. In some cases, the relaxation time τ exhibits an activation-type temperature dependence, whose activation energy corresponds to an energy barrier between the two stable states, and τ becomes much longer than 1 s at low temperatures. In magnetic nanoparticles and magnetic molecules [1–6], the spins in one component (particle or molecule) are strongly coupled and form a large spin, but there is only a weak magnetic interaction between the components, and the magnetic anisotropy is the origin of the activation energy. In the case of diluted magnets or geometrically frustrated magnets [7–11], spin fluctuation arising from disorder or frustration plays an important role in the relaxation behavior. For the magnets exhibiting a meta-magnetic phase transition [12–19], the magnetic relaxation is observed only near the phase boundary by tuning the magnetic field, temperature, or composition of the compounds, and the spin-lattice coupling is likely to play an important role in the formation of the energy barrier and the magnetic relaxation.

La$_5$Mo$_4$O$_{16}$ [20–26] has a layered structure with Mo square lattices along the ab plane. There are two inequivalent Mo sites in the square lattice, Mo1 and Mo2, which are occupied by Mo^{5+} ($4d^1$, $S = 1/2$) and Mo^{4+} ($4d^2$, $S = 1$), respectively, and have a checkerboard-type alignment. Each layer of the Mo square lattice is separated from the neighboring layer by a block including nonmagnetic Mo ions, and thus it can be regarded as a two-dimensional magnet. A recent study on a single crystal grown by fused salt electrolysis [26] has shown that this compound exhibits an antiferromagnetic ordering at $T_{AF} \sim 190$ K. In this antiferromagnetic phase, the $S = 1/2$ spins on the Mo1 sites and $S = 1$ spins on the Mo2 sites order antiferromagnetically, resulting in a ferrimagnetic moment on a Mo square lattice, and the ferrimagnetic moment in each layer is aligned alternately along the c axis (perpendicular to the layer), resulting in an interlayer antiferromagnetic state.

In addition to such an antiferromagnetic ordering, it was reported that there is a ferromagnetic phase when a magnetic field of $H > 0.5$ T is applied along the c axis, or even without a magnetic field below $T_F \sim 70$ K [26]. In this ferromagnetic phase, it is suggested that the ferrimagnetic moment in each layer is aligned ferromagnetically along the c axis (an interlayer ferromagnetic state). The magnetization curve as a function of the magnetic field exhibits a hysteresis loop typical of a ferromagnetic state below 70 K, whereas it exhibits a sharp increase at ~ 0.5 T above 70 K, indicating a metamagnetic phase transition [26]. This means that the magnetic interaction between the layers is extremely weak (less than 1 K) in this compound.

In this Rapid Communication, we studied the magnetic properties of La$_5$Mo$_4$O$_{16}$ and Co-doped samples in detail, and we found that the "ferromagnetic" phase below 70 K in a zero magnetic field is not a ground state but a metastable state with a long relaxation time. The unusual characteristics in the relaxation of the magnetization in a pure crystal magnet are discussed.

Single crystals of La$_5$Mo$_4$O$_{16}$ and La$_5$Mo$_{4-x}$Co$_x$O$_{16}$ were grown by fused salt electrolysis. The Co concentration of several samples was determined by electron probe microanalysis, and the Co concentration of other samples was estimated by assuming that the amount of Co in the starting material is proportional to the Co concentration in the crystal. The magnetization was measured by a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS3). In the following, the magnetic field is applied along the c direction (perpendicular to the Mo square lattice).

Figure 1(a) shows the temperature (T) dependence of the magnetization (M) at 0.1 T in a warming run after cooling the sample with an applied magnetic field of 5 T. T_{AF}, at which a cusp appears in $M(T)$, decreases with increasing Co concentration, as more clearly seen in the inset. Furthermore, the absolute value of M at low T increases with increasing Co concentration. It is likely that the magnetic interaction between the Mo spin and the Co spin is ferromagnetic, which leads to a decrease in T_{AF} and an increase in M at low T.

In contrast, T_F, above which $M(T)$ sharply decreases, barely changes with Co doping, as shown in Fig. 1(a). The x dependences of T_{AF} and T_F are summarized in Fig. 1(b). T_F should be considered as the temperature at which the interlayer magnetic interaction changes from antiferromagnetic with the absolute value of <1 K to ferromagnetic. However, it is unlikely that such behaviors presumably caused by a subtle

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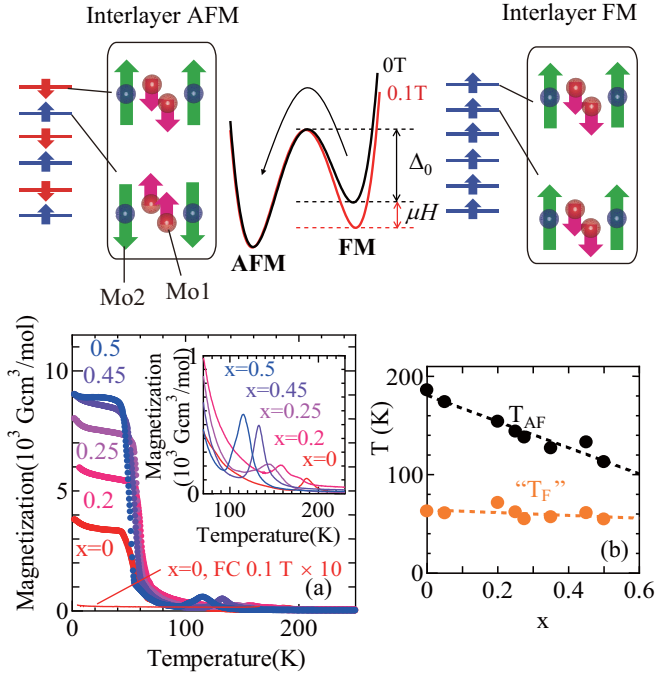T. KONISHI, K. KOBAYASHI, AND T. KATSUFUJI

FIG. 1. (Color online) Upper panel: Schematic picture of the interlayer antiferromagnetic state (left) and the interlayer ferromagnetic state (right), together with a schematic picture of the free energy (middle). (a) Temperature dependence of the magnetization for $La_5Mo_{4-x}Co_xO_{16}$ at 0.1 T in a warming run after cooling the samples in an applied magnetic field of 5 T. The thin solid line corresponds to that measured in a cooling run at 0.1 T for $x = 0$ (multiplied by 10). The inset is an expanded figure between 70 and 230 K. (b) The x dependences of T_{AF} and T_F for $La_5Mo_{4-x}Co_xO_{16}$.

FIG. 2. (Color online) (a)–(c) Time dependence of the magnetization for $La_5Mo_4O_{16}$ at various temperatures at (a) $H_0 = 0$, (b) 0.05, and (c) 0.1 T. (d) Time dependence of the magnetization at various values of H_0 at 40 K.

balance of the interactions is unaffected when the average antiferromagnetic interaction within the layer, which is of the order of 100 K, changes and T_{AF} decreases by 40% as a result of Co doping. It should be pointed out again that $M(T)$ was measured after cooling the sample in an applied magnetic field of 5 T. Although this is a typical method of measuring the spontaneous magnetization of a ferromagnet with a large coercive field, this process of magnetization measurement may not correctly reflect the ground state of the samples, but may detect a magnetic-field-induced phase.

To investigate this possibility, we measured the relaxation of the magnetization for $La_5Mo_4O_{16}$ and $La_5Mo_{3.65}Co_{0.35}O_{16}$. First, the temperature of the sample was increased to above T_{AF}, and then it was decreased to T_0 ($<T_{AF}$) in an applied magnetic field of 5 T, with the sample in the ferromagnetic state. Then, H was decreased to $H_0 = 0$, 0.05, or 0.1 T, and M was measured as a function of time t while fixing H to H_0 and T to T_0.

Figures 2(a)–2(c) show the time dependence of the magnetization for $La_5Mo_4O_{16}$ at various temperatures at $H_0 = 0$, 0.05, and 0.1 T, respectively, and Fig. 2(d) shows the time dependence at various values of H_0 at a fixed T of 40 K. The corresponding results for $La_5Mo_{3.65}Co_{0.35}O_{16}$ are shown in Fig. 3. In all the figures, M is normalized by the value at $t = 0$. As can be seen, M gradually decreases with increasing t for 30–50 K. This relaxation behavior has several characteristics:
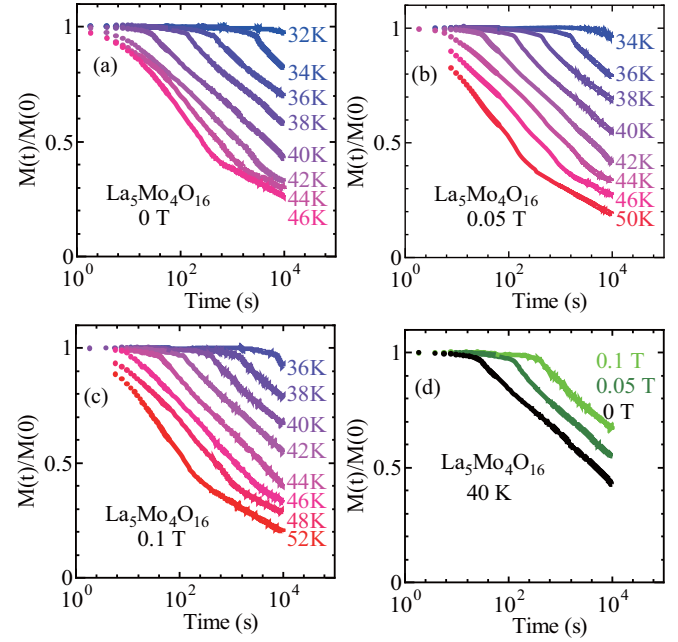
(1) The relaxation time increases with decreasing T. (2) The relaxation time increases with increasing H_0. (3) All the curves of M vs $\log t$ appear to merge if each curve is shifted by a certain value of $\log t$.

We found that the $M(t)$ curve itself cannot be fitted by a single relaxation function nor the stretched exponential
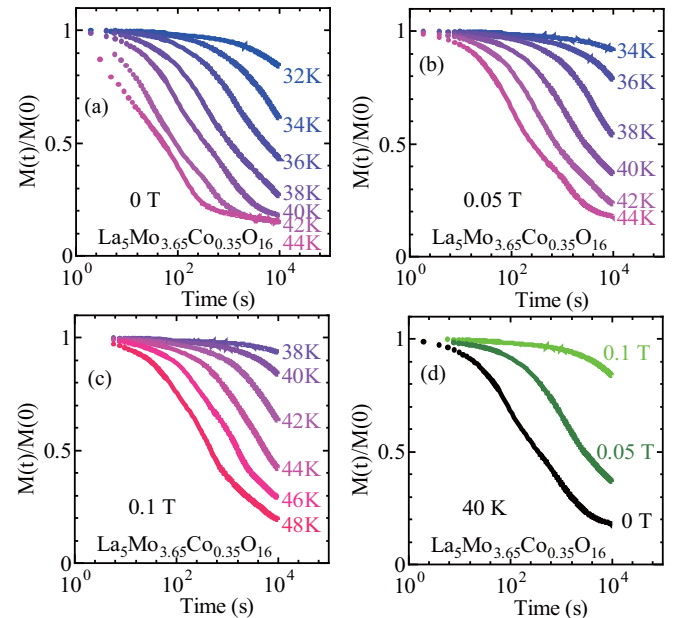

FIG. 3. (Color online) (a)–(c) Time dependence of the magnetization for $La_5Mo_{3.65}Co_{0.35}O_{16}$ at various temperatures at (a) $H_0 = 0$, (b) 0.05, and (c) 0.1 T. (d) Time dependence of the magnetization at various values of H_0 at 40 K.
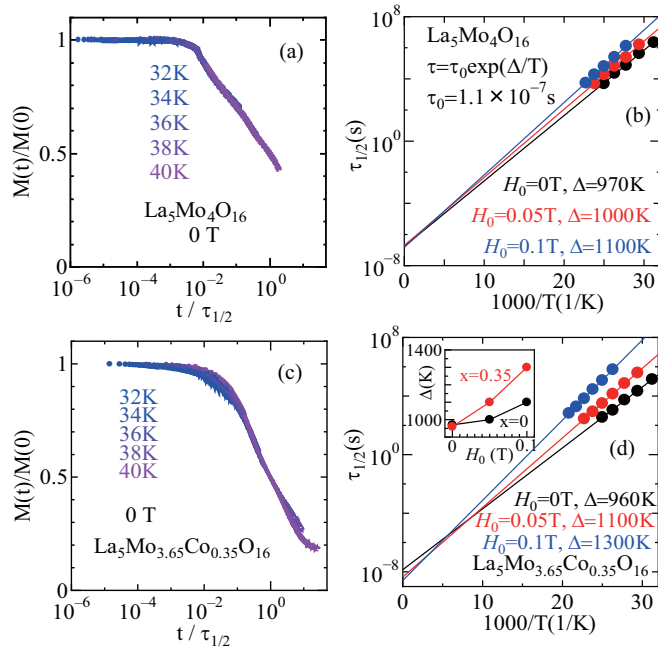
FIG. 4. (Color online) (a), (c) Scaling plot of the magnetization as a function of time divided by $\tau_{1/2}$ for (a) $La_5Mo_4O_{16}$ and (c) $La_5Mo_{3.65}Co_{0.35}O_{16}$. (b), (d) Arrhenius plot of $\tau_{1/2}$ obtained by scaling analysis at various values of H_0 for (b) $La_5Mo_4O_{16}$ and (d) $La_5Mo_{3.65}Co_{0.35}O_{16}$. The inset of (d) shows the H_0 dependence of Δ for $x = 0$ and 0.35.

behavior $M_0 \exp[-(t/\tau)^\beta]$ [27]. Nevertheless, we can estimate a typical time scale that corresponds to τ in the relaxation function at each T by using characteristic (3) above. This means that the scaling relation $M(t)/M(0) = f(t/\tau_{1/2})$ holds, where $f(x)$ is a universal function independent of T and $f(1) = 1/2$, with an appropriate choice of $\tau_{1/2}$ at each T. Note that $\tau_{1/2}$ is the time at which M becomes half the value at $t = 0$ and corresponds to the relaxation time. Figure 4(a) shows such a scaling plot of $M(t)/M(0)$ vs $t/\tau_{1/2}$ for $La_5Mo_4O_{16}$ with $H_0 = 0$ T. As can be seen, the data between 32 and 40 K merge to a single function. Figure 4(b) shows the Arrhenius plot of $\tau_{1/2}$ vs T (T_0); $\tau_{1/2}$ for $H_0 = 0$ T exhibits activation-type behavior, $\tau_{1/2} = \tau_0 \exp(\Delta/k_B T)$ with $\Delta/k_B = 970$ K and $\tau_0 \sim 1.1 \times 10^{-7}$ s. It was found that $M(t)/M(0)$ for $H_0 = 0.05$ and 0.1 T also exhibits scaling behavior and $\tau_{1/2}$ has activation-type behavior, as shown in Fig. 4(b). The activation energy Δ increases with increasing H_0, whereas τ_0 remains at approximately $\sim 1.1 \times 10^{-7}$ s.

Similar results were obtained for $La_5Mo_{3.65}Co_{0.35}O_{16}$, as shown in Fig. 3. $M(t)/M(0)$ vs $t/\tau_{1/2}$ merge to a single function for $H_0 = 0$ [Fig. 4(c)], 0.05, and 0.1 T. $\tau_{1/2}$ as a function of T_0 also exhibits activation behavior, as shown in Fig. 4(d). One of the differences between the result for the pure compound and that for the Co-doped compound is that the change in the $M(t)/M(0)$ curve with the applied magnetic field H is more substantial for the Co-doped sample, as exemplified in Figs. 2(d) and 3(d). This leads to a larger increase in Δ with H_0 for the Co-doped compound, as shown in the inset of Fig. 4(d).

These experimental results imply that there is no phase transition from the interlayer antiferromagnetic state to the interlayer ferromagnetic state at zero magnetic field. The change in $M(T)$ at 70 K shown in Fig. 1(a) arises from the fact that the relaxation time (from a magnetic-field-induced ferromagnetic phase to an antiferromagnetic phase) decreases with increasing T and becomes comparable to the time scale of the measurement (several seconds) at ~ 70 K. The hysteresis loop of $M(H)$ below 70 K also arises from the fact that the time scale for the sweeping of the magnetic field is shorter than the relaxation time in this T range.

In comparison with other magnets exhibiting magnetic relaxation, there are several unique aspects for the present compounds. The experimental result that the pure and Co-doped compounds exhibit similar relaxation behavior with almost the same relaxation time indicates that disorder does not play a principal role in the relaxation process of $La_5Mo_4O_{16}$ [28]. Also, this result indicates that the activation energy Δ in the T dependence of the relaxation time, which corresponds to the height of the energy barrier between the two states, is dominated by an intrinsic parameter of the compounds. Furthermore, the relaxation is observed at 30–50 K, which is much lower than the antiferromagnetic ordering temperature $T_{AF} = 190$ K, indicating that the relaxation occurs almost in the absence of spin fluctuations.

The magnetic properties of $La_5Mo_4O_{16}$ have several characteristics. First, magnetism is highly two dimensional. $T_{AF} = 190$ K means that the antiferromagnetic interaction within a layer of the Mo square lattice ($J_\parallel$) is ~ 100 K [29]. On the other hand, the fact that the magnetic field of 0.5 T causes a transition from an interlayer antiferromagnetic state to an interlayer ferromagnetic state means that the interlayer magnetic interaction ($J_\perp$) is ~ 0.13 K; thus the anisotropy amounts to almost three orders of magnitude. Furthermore, the Mo spins have a large magnetic anisotropy with the easy axis normal to the layer (Ising-type anisotropy), which is confirmed by the experimental result that a magnetic field of 5 T parallel to the layer can induce a much smaller magnetization below T_{AF} [26]. This means the relation $J_\parallel \gg K > J_\perp$, where K is the magnetic anisotropy energy of the Mo spin.

Because of the two-dimensional character of the magnet, the magnetic moments in $La_5Mo_4O_{16}$ are strongly coupled within a layer by $J_\parallel$, and the ferrimagnetic moment in each layer can be regarded as a big spin, the size of which (S) is given by the moment of each Mo spin (s) multiplied by the total number of Mo spins coupled within the same layer (N), $S = Ns$. Such a big spin S is only extremely weakly antiferromagnetically coupled with the big spin in the next layer by $NJ_\perp$. When a big spin S is flipped to the opposite direction, there is an energy barrier Δ to overcome, which is approximately given by NK. The relation $J_\parallel \gg K > J_\perp$ means that the energy barrier $\Delta = NK$ is higher than the energy difference between the interlayer-ferromagnetic state and the interlayer-antiferromagnetic state given by $NJ_\perp$, and thus the relaxation between the two states, as illustrated in the upper panel of Fig. 1, occurs. This scenario can explain the unique aspects of $La_5Mo_4O_{16}$ discussed above.

One of the experimental results that supports this scenario is that Δ/k_B for $La_5Mo_4O_{16}$ increases upon applying a magnetic field, as shown in the inset of Fig. 4(d). According to the simple

relationship between the energy and the magnetic field, the height of the energy barrier changes as $\Delta = \Delta_0 + \mu H$ (Fig. 1), where Δ_0 is the height of the energy barrier at zero magnetic field and μ is the size of the magnetic moment. The slope of the Δ vs H in the inset of Fig. 4(d) indicates that μ is the order of $\sim 10^3 \mu_B$, which is consistent with the idea that a large number of Mo spins are coupled within the layer and act as a big spin ($N \sim 10^3$). The larger slope (and larger μ) in the Co-doped compound should be attributed to the larger magnetic moment of the Co ions and the larger ferrimagnetic moment [Fig. 1(a)].

Comparing the present compounds with magnetic nanoparticles or magnetic molecules, each layer in the present system corresponds to each particle or molecule, and the extremely weak interlayer interaction corresponds to the interparticle or intermolecular interaction. An advantage of the present system is that there are two distinct interlayer arrangements of the spins, ferromagnetic and antiferromagnetic, which are separated by an energy barrier, and the energies of the two states and the height of the energy barrier can be controlled by applying a magnetic field. Comparing the present compounds and the magnets exhibiting a relaxation near the metamagnetic transition, the relaxation occurs in the limited ranges of the temperature, the magnetic field, and the composition in the latter case, since the energy difference between the two magnetic states and the height of the energy barrier in between are dominated by various issues, including the spin-lattice coupling. For $La_5Mo_4O_{16}$, they are dominated only by the intrinsic parameters of the magnetism, $J_\perp$ and K, and thus the relaxation is observed in the wide ranges of the temperature and the composition.

There are two issues to be discussed: (1) What determines N ($\sim 10^3$), the number of spins coupled within a layer? (2) What determines τ_0 ($\sim 10^{-7}$–10^{-8} s), the relaxation time in the high-T limit? Regarding (1), it should be emphasized again that N is determined by the intrinsic properties of the compounds and not by extrinsic disorder or other effects. Note that the number of Mo ions in one layer in the actual crystal is much larger than 10^3. However, when a large number (N)

of Mo spins are coupled and rotate simultaneously, the total energy required to overcome the magnetic anisotropy energy K for N spins should be smaller than the energy required to rotate each Mo spin independently, which is dominated by the intralayer magnetic interaction $J_\parallel$. Thus, it is most likely that N is determined by the ratio of $J_\parallel$ to K, although its functional form has yet to be clarified.

Regarding (2), τ_0 should be of the order of $\hbar/\Delta \sim 10^{-14}$ s with $\Delta/k_B \sim 1000$ K based on a conventional discussion of the relaxation process, which is several orders of magnitude smaller than the experimental result. In the case of magnetic molecules, where all the spins in one molecule are coupled and form a single spin with a large spin number S, the energy barrier Δ is composed of the multiple states corresponding to the eigenstates of S_z [30]. Thus, the relaxation process includes the cascade of transitions between such spin eigenstates, which leads to a relaxation time much longer than $\hbar/\Delta$. This can be applied to the present case, where the energy barrier $\Delta \sim NK$ is composed of the multiple states.

In summary, we found that a layered magnet $La_5Mo_4O_{16}$ and a Co-doped sample exhibit a relaxation of the magnetization when the system changes from a metastable ferromagnetic state to an antiferromagnetic ground state. The relaxation time has an activation-type temperature dependence with an activation energy of ~ 1000 K, and a relaxation time at the high-temperature limit of $\sim 10^{-7}$–10^{-8} s, irrespective of Co doping. This long-time relaxation arises from the relatively strong magnetic interaction within a layer and the extremely weak magnetic interaction between the layers in this compound. Because of such a huge anisotropy of the magnetic interaction, the Mo spins are strongly coupled and form a "big" spin within a layer, and these big spins weakly interact between the layers with a magnetic anisotropy energy that acts as an energy barrier in the thermal activation process.

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[27] See Supplemental Material at http://link.aps.org/supplemental/ 10.1103/PhysRevB.92.020419 for the fitting of $M(t)$ by the sum of several relaxation functions, the sweep rate dependence of M versus temperature, and the relaxation behavior from the antiferromagnetic to the ferromagnetic phase.

[28] It is reasonable to assume that the substitution of the Mo ions by magnetic Co ions is the effective introduction of disorder as a magnet, and thus the Co-doped compound has a larger amount of disorder than the parent compound, in which the oxygen vacancies are the possible origin of disorder.

[29] According to a mean-field approximation of the Hamiltonian $\Sigma J_\parallel \boldsymbol{S}_i \cdot \boldsymbol{S}_j + J_\perp \boldsymbol{S}_i \cdot \boldsymbol{S}_j$, assuming a strong Ising anisotropy for the $S = 1$ spin in the Mo^{4+} ion, $k_B T_{AF} = 2J_\parallel$ and $g\mu_B H_c = 5J_\perp$, where H_c is the magnetic field at which the magnetic state changes from the interlayer antiferromagnetic to the interlayer ferromagnetic state. $T_{AF} = 200$ K and $H_c = 0.5$ T give $J_\parallel = 100$ K and $J_\perp = 0.13$ K. Note that there are two interlayer magnetic interactions, between Mo^{5+} ($S = 1/2$) and Mo^{5+} ($S = 1/2$), and between Mo^{4+} ($S = 1$) and Mo^{4+} ($S = 1$), and we cannot separately obtain the magnitude of these two interactions from the experiment. Here, we assume that $J_\perp$ is the same in both cases, and thus the energy differences between the ferromagnetic and antiferromagnetic configurations are four times different.

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